



If  $a'$  is the hydrogen bromide consumed by the first dealkylation and  $a''$  that by the second in time  $t$ , then

$$a = a_0 - a' - a'' \quad \dots \quad (3)$$

and at later stages  $a' \approx b_0$ .

Hence 
$$-da/dt = k_2 a(a' - a'') \\ = k_2 a(2b_0 - a_0 + a) \quad \dots \quad (4)$$

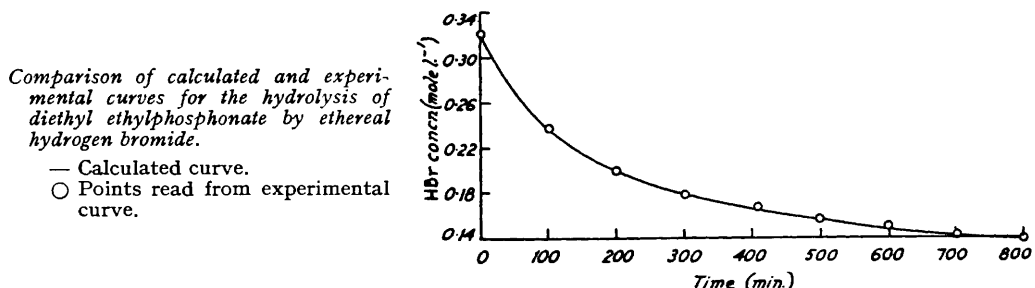
Integrating, we have :

$$\frac{1}{2b_0 - a_0} \log \left( \frac{2b_0 - a_0 + a}{a} \cdot \frac{a_0}{2b_0} \right) = k_2 t \quad \dots \quad (5)$$

For the special case of initially equimolecular concentrations  $a_0 = 2b_0$ , we have

$$1/a - 1/a_0 = k_2 t \quad \dots \quad (6)$$

It is also possible to extend Frost and Schwemer's tables (*loc. cit.*) for cases where  $k_1 > 10k_2$ . This laborious procedure was performed and compared for typical cases with the method given above. The equality of results demonstrated the reliability of the methods.



The middle part of the reaction curve was not used in evaluation of rate constants when  $k_1/k_2 > 10$ . It is worth investigating if the values of  $k_1$  and  $k_2$  do supply a calculated rate in this region in agreement with experiment. This can be done by utilising Frost and Schwemer's equation (7) :

$$\tau = \frac{1 - \kappa}{1 - 2\kappa} \int_{\beta}^1 \frac{d\beta}{\beta^2 [1 + \beta^{\kappa-1}/(1 - 2\kappa)]} \quad \dots \quad (7)$$

where  $\beta = b/b_0$ ,  $\kappa = k_2/k_1$  and  $\tau = b_0 k_1 t$ . For  $\kappa$  determined from initial and final stages, graphical integration of (7) for various values of  $\beta$  was performed to give corresponding values of  $\tau$ . For each value of  $\beta$ , the value of  $\alpha = a/a_0$  was found by Frost and Schwemer's equation (10) :

$$\alpha = [(1 - 2\kappa)/2(1 - \kappa)]\beta + [1/2(1 - \kappa)]\beta^{\kappa}$$

Hence, since  $\alpha$  and  $\tau$  are known, a calculated line of  $\alpha$  versus  $t$  could be drawn for appropriate values of  $a_0$ . The fit was very satisfactory (see Figure).

Frost and Schwemer's analysis was devised to obtain rate constants for cases where  $k_1 < 10k_2$ . The times required to reach specified extents of reaction are measured, and several ratios taken, e.g., the times required for 60% and for 30% reaction. These ratios are obviously dependent on the relative values of  $k_1$  and  $k_2$ . Tables are provided for using these ratios and absolute times of reaction so as enable  $k_1$  and  $k_2$  to be read off. For various ratios, with one initial equimolecular concentration and for various initial equimolecular concentrations, constant values for  $k_1$  and  $k_2$  were obtained for the stepwise dealkylations mentioned.

#### EXPERIMENTAL

*Preparation of Esters.*—Dialkyl alkylphosphonates were prepared from the corresponding trialkyl phosphites and an alkyl halide, by the Arbuzov reaction (*J. Russ. Phys. Chem. Soc.*, 1906, **38**, 687) and were purified by careful fractionation. Diethyl ethylphosphonate had b. p.  $82^{\circ}/10$  mm.,  $n_D^{20}$  1.4168 (Found : P, 18.75. Calc. for  $C_6H_{15}O_3P$  : P, 18.7%). Diethyl *n*-octylphosphonate had b. p.  $83^{\circ}/0.02$  mm.,  $n_D^{18}$  1.4353 (Found : P, 12.4. Calc. for  $C_{12}H_{27}O_3P$  : P,

12.4%). Diethyl 1-phenylethylphosphonate (prepared as described by Gerrard and Green, *loc. cit.*) had b. p. 88°/0.05 mm.,  $n_D^{18}$  1.4870 (Found: P, 12.7. Calc. for  $C_{13}H_{19}O_3P$ : P, 12.8%). *Di-n-propyl ethylphosphonate* had b. p. 112°/15 mm.,  $n_D^{20}$  1.4238 (Found: C, 49.5; H, 9.80; P, 16.0.  $C_8H_{19}O_3P$  requires C, 49.5; H, 9.85; P, 15.95%). *Diisopropyl ethylphosphonate* had b. p. 90°/19 mm.,  $n_D^{20}$  1.4122 (Found: P, 16.1.  $C_8H_{19}O_3P$  requires P, 15.95%). Diethyl acetylphosphonate, b. p. 110°/17 mm.,  $n_D^{17}$  1.4240 (Found: P, 17.25. Calc. for  $C_6H_{13}O_4P$ : P, 17.2%), was prepared by Kabachnik and Rossiiskaya's method (*Isvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, 1945, 364), but our yield of 78% was considerably better than theirs. Diethyl hydrogen phosphite, b. p. 82°/18 mm.,  $n_D^{18}$  1.4100 (Found: P, 22.6. Calc. for  $C_4H_{11}O_3P$ : P, 22.45%), was prepared as described by Gerrard (*J.*, 1940, 1464). Triethyl phosphate had b. p. 102—103°/15 mm.,  $n_D^{20}$  1.4061 (Found: P, 17.0. Calc. for  $C_6H_{15}O_4P$ : P, 17.0%).

The solvent used in the kinetic runs was the best grade of ether, and was distilled from sodium before use.

*Method and Apparatus.*—Hydrogen bromide and the phosphonate in ethereal solution were allowed to react in a thermostat. A solution of hydrogen bromide was first prepared by passing the dry gas into the ether, and the approximate concentration of the solution was determined. This stock solution was then diluted with more solvent, to a known volume, to give approximately the concentration required, and its exact molarity determined. The stoichiometrically equivalent weight of ester and the final molarities were calculated, after allowance for the volume change on the addition of the ester. Samples were removed after specified time intervals, by the application of dried air under pressure to the surface of the solution. The solution was forced up an exit tube, through a tap, and into a sampler of known volume, also fitted with taps at each end. The bromide ion, in the aqueous extract of each sample, was determined by Volhard's method.

*Results.*—Three typical runs are reported in Tables 1, 4, and 6.

TABLE 1. (a) *Diethyl ethylphosphonate (0.1605M) and hydrogen bromide (0.3205M) at 25.0°.*

Time (min.)	2	15	30	60	100	180
HBr concn. ( $10^{-3}$ mole l. <sup>-1</sup> )	318.5	302.5	283.5	261	238	206.5
Time (min.)	245	320	408	1360	1682	2757
HBr concn. ( $10^{-3}$ mole l. <sup>-1</sup> )	190	176.5	166	118	112	96
Time (min.)	4290	6075	8360	9840		
HBr concn. ( $10^{-3}$ mole l. <sup>-1</sup> )	76	63	49.5	46		

(a) (See Table 1.) From the smooth curve drawn on a large scale through the experimental points, the hydrogen bromide concentrations at equal intervals of time were read for the first half of the complete reaction. The corresponding ester concentrations were calculated, neglecting the second reaction, and a graph of  $\log ([HBr]/[Ester])$  versus time was plotted. The data in Table 2 were thus used.

TABLE 2.

Time (min.)	0	20	40	60	80	100	120
$\log ([HBr]/[Ester])$	0.300	0.339	0.378	0.412	0.448	0.485	0.521
Time (min.)	140	160	180	220	260	300	340
$\log ([HBr]/[Ester])$	0.559	0.601	0.646	0.741	0.843	0.958	1.094

From the initially linear slope,  $k_1$  (the second-order specific rate for the first dealkylation) was calculated to be  $4.43 \times 10^{-4}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. A curve of hydrogen bromide concentration versus time was also drawn for the whole reaction, and hydrogen bromide concentrations at larger time intervals read off. A graph of  $\log 1/[HBr]$  versus time was plotted (see Table 3).

TABLE 3.

Time (min.)	500	1000	2000	3000	4000	5000	6000	7000	8000	9000
$1/[HBr]$ (l. mole <sup>-1</sup> )	6.33	7.69	9.40	11.0	12.7	14.3	15.9	17.5	19.4	20.8

TABLE 4. (b) *Diethyl n-octylphosphonate (0.0730M) and hydrogen bromide (0.1460M) at 25.0°.*

Time (min.)	3	16	40	86	147	206	250	305	380	460
HBr concn. ( $10^{-3}$ mole l. <sup>-1</sup> )	145	140.5	133	122	115	107.5	104	100	95	91
Time (min.)	1182	1408	1825	3085	5850	8630	14,620	20,150	24,750	
HBr concn. ( $10^{-3}$ mole l. <sup>-1</sup> )	72.5	70.5	67	59.5	51.5	45	39	33	31	

The slope of the linear part of this curve was equal to  $k_2$  (the second-order specific rate for the second dealkylation) =  $2.65 \times 10^{-5}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. The ratio  $k_1/k_2$  was thus 16.7.

TABLE 5.

Time (min.)	0	20	60	100	140	180	220	260	300
log ([HBr]/[Ester])...	0.301	0.325	0.365	0.401	0.433	0.468	0.503	0.536	0.570
Time (min.)	340	380	420	460					
log ([HBr]/[Ester])...	0.603	0.637	0.670	0.698					
Time (min.)	2000	4000	6000	8000	10,000	12,000	14,000	18,000	22,000
1/[HBr] (l. mole <sup>-1</sup> )...	15.2	17.7	19.4	20.8	22.2	23.6	25.0	28.2	30.8

(b) (See Table 4.) Graphs of log [HBr]/[Ester] and 1/[HBr] versus time were plotted as before, with the results given in Table 5. The value of  $k_1$  was  $4.45 \times 10^{-4}$  and of  $k_2$   $1.22 \times 10^{-5}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>. The ratio  $k_1/k_2$  in this case was 36.5, and hence the deviation from linearity of the log [HBr]/[Ester] plot develops much later.

TABLE 6. (c) *Diethyl acetylphosphonate (0.1095M) and hydrogen bromide (0.2180M) at 25.0°.*

Time (min.)	2	17	30	69	131	197	275	351
$\alpha = [HBr]/[HBr]_0$ ...	0.996	0.985	0.969	0.940	0.892	0.849	0.792	0.732
Time (min.)	445	504	1400	1715	2025	2810	4290	5970
$\alpha = [HBr]/[HBr]_0$ ...	0.691	0.678	0.429	0.383	0.346	0.275	0.188	0.141

(c) (See Table 6.)  $\alpha$  versus time was plotted on a large scale, and times of 20% up to 60% reaction were read. The "t" ratios were calculated and by interpolation in the prepared tables of Frost and Schwemer the corresponding values of  $1/\kappa$  were found. From the average  $1/\kappa$  value, the values of  $\tau$  were also found from the tables, and  $k_1$  and hence  $k_2$  were calculated. Results are in Tables 7 and 8.

TABLE 7.

Reaction (%)	t (min.)	Percentage compared	"t" ratio	1/κ	Reaction (%)	t (min.)	Percentage compared	"t" ratio	1/κ
20	265	60/20	6.038	2.046	50	1063	60/50	1.506	2.092
30	450	60/30	3.556	2.145	60	1600	50/20	4.012	2.030
40	715	60/40	2.248	2.000			50/30	2.363	2.181

Average  $1/\kappa = 2.08$

TABLE 8.

Reaction (%)	20	30	40	50	60
$\tau$	0.2510	0.4311	0.6727	1.012	1.523
$10^{-4}k_1$ (l. mole <sup>-1</sup> sec. <sup>-1</sup> )	1.446	1.462	1.436	1.453	1.453

Average  $k_1 = 1.45 \times 10^{-4}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>.

Average  $k_2 = 1.45 \times 10^{-4}/2.08 = 6.97 \times 10^{-5}$  l. mole<sup>-1</sup> sec.<sup>-1</sup>.

The rate constants obtained for the various esters, in ethereal solution, are summarised in Table 9.

TABLE 9.

Ester	Initial concn. (mole l. <sup>-1</sup> )		Rate constants (l. mole <sup>-1</sup> sec. <sup>-1</sup> )		$k_1/k_2$ *
	HBr	Ester	$10^4k_1$	$10^5k_2$	
Et·PO <sub>3</sub> Et <sub>2</sub>	0.3205, 0.1485	0.1605, 0.0750	4.43, 4.27	2.65, 2.50	17.2
	0.1880, 0.0710	0.0940, 0.0355	4.26, 4.33	2.35, 2.64	
Et <sub>2</sub> HPO <sub>3</sub>	0.3945, 0.2400	0.1970, 0.1200	4.73, 4.45	3.44, 3.50	13.1
n-C <sub>4</sub> H <sub>9</sub> ·PO <sub>3</sub> Et <sub>2</sub>	0.1340, 0.1460	0.0670, 0.0730	4.30, 4.45	1.31, 1.22	34
CHPhMe·PO <sub>3</sub> Et <sub>2</sub>	0.2070, 0.1270	0.1070, 0.0635	3.37, 3.07	1.38, 1.33	23
Ac·PO <sub>3</sub> Et <sub>2</sub>	0.1960, 0.2180	0.0980, 0.1095	1.37, 1.45	6.56, 6.97	2.1
Et·PO <sub>3</sub> Pr <sup>n</sup> <sub>2</sub>	0.3045, 0.1895	0.1525, 0.0950	3.56, 3.78	1.23, 1.31	28
Et·PO <sub>3</sub> Pr <sup>n</sup> <sub>1</sub>	0.2200, 0.1380	0.1105, 0.0690	0.933, 0.986	0.880, 0.917	10.7
Et <sub>2</sub> PO <sub>4</sub>	0.1710	0.0855	9.02	7.13	12.7
Et <sub>2</sub> HPO <sub>3</sub> at 15.0°	0.1575, 0.1540	0.0785, 0.0775	0.921, 0.924	1.72, 1.73	5.4
Et·PO <sub>3</sub> Et <sub>2</sub> at 15.0°	0.1767	0.0825	1.38	0.68	20.3
Et <sub>2</sub> PO <sub>4</sub> at 15.0°	0.3130	0.1040	3.12	3.06	10.2
Et <sub>2</sub> HPO <sub>3</sub> at 20.0°	0.1100	0.0660	1.95	—	—

\* From average values of  $k_1$  and  $k_2$ .

## DISCUSSION

In each example the dealkylation was clearly of the second order; but because the observations were all for ethereal solutions, and the influence of ether has not yet been decided, a detailed discussion on mechanism must be postponed until data for other solvents and conditions are available. It is possible that, even if competitive complex-formation between hydrogen bromide and ether did not complicate the kinetics, it might still affect the values of the rate constants. Ether was chosen because of the convenient solubility of hydrogen bromide. Nevertheless the results provide a quantitative comparison of the influence of structure on the first and the second dealkylation, and also clearly show the degree of control which may be held over the steps of dealkylation.

Replacement of hydrogen by an ethyl or *n*-octyl group in the compound  $\text{O:PH(OEt)}_2$  has little effect on  $k_1$  (the first dealkylation), but has more effect on  $k_2$  (the second one), and increases the ratio  $k_1/k_2$ . Thus for diethyl hydrogen phosphite  $k_1/k_2$  is 13.1, for diethyl ethylphosphonate 17.2, and for diethyl *n*-octylphosphonate 34. These ratios indicate to what extent dealkylation may be restricted to the first group, and so lead to the convenient preparation of the acid esters. Ethyl hydrogen *n*-octylphosphonate,  $\text{O:PR(OEt)(OH)}$ , was obtained in this way by Cooke, Gerrard, and Green (*Chem. and Ind.*, 1953, 351). In view of the great reactivity of the 1-carbon atom in 1-phenylethanol (cf. Gerrard, *J.*, 1944, 88; Gerrard and Shepherd, *J.*, 1953, 2069), the difference between  $k_1$  ( $3.2 \times 10^{-4}$ ) for diethyl 1-phenylethylphosphonate and  $k_1$  ( $4.3 \times 10^{-4}$ ) for diethyl hydrogen phosphite appears surprisingly small. The acetyl group has a more marked effect:  $k_1 = 1.4 \times 10^{-4}$ , but  $k_2$  is larger than for the hydrogen phosphite, making  $k_1/k_2 = 2$ . For such an ester, the production of the acid ester will be very much less efficient.

Replacement of the ester ethyl group by *n*-propyl,  $\text{O:PEt(OEt)}_2 \longrightarrow \text{O:PEt(OPr}^n)_2$ , caused a slight reduction in  $k_1$ , and a greater one in  $k_2$ , thus increasing the ratio  $k_1/k_2$  to 28. Replacement by *isopropyl*, to give  $\text{O:PEt(OPr}^i)_2$ , causes a considerable reduction in  $k_1$  ( $0.96 \times 10^{-4}$ ), but a smaller reduction in  $k_2$ , lowering the ratio  $k_1/k_2$  to 11.

For triethyl phosphate,  $k_1$  and  $k_2$  are both twice as large as for diethyl hydrogen phosphite. This could be due in some measure to the statistical availability of alkyl groups.

In the types of ester studied, the phosphorus atom is quinquevalent and of the general structure  $\text{O:PX(OR)}_2$ , where  $\text{X} = \text{H, OR, or R, or R'}$ ; but a trialkyl phosphite,  $\text{P(OR)}_3$ , contains a trivalent phosphorus atom, and the much greater rate of the first dealkylation,  $\text{P(OR)}_3 + \text{HBr} \longrightarrow \text{O:PH(OR)}_2 + \text{RBr}$ , may be partly attributed to a tendency for phosphorus to attain quinquecovalency. It was found by Gerrard and Whitbread (*loc. cit.*) that, in 0.2M-concentration and with hydrogen bromide, tri-*n*-butyl phosphite was completely dealkylated to dibutyl hydrogen phosphite in 7 minutes at  $-11^\circ$ . Of relevance is the fact that in the examples of alcohols of ordinary reactivity it is the dialkyl hydrogen phosphite, and never the trialkyl phosphite, which can be obtained by the interaction of the alcohol and phosphorus trichloride.

We thank Dr. W. F. Watson for helpful discussions.

THE NORTHERN POLYTECHNIC,  
HOLLOWAY ROAD, LONDON, N.7.

[Received, February 7th, 1955.]